



Stirring or milling? First synthesis of Rh(I)-(di-N-heterocyclic carbene) complexes both in solution and in a ball mill

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ABSTRACT

An environment-friendly, convenient, fast and solvent-free mechanochemical approach have been accomplished for the synthesis of several diimidazolium salts and the bridging dinuclear rhodium(I)-N-heterocyclic carbene complexes of the type $[\{\text{RhCl}(\text{cod})\}_2(\mu\text{-di-NHC})]$ derived from them. The compounds were synthesized also by the classical solvent method and the results of the two approaches were compared. A systematic study of both the mechanochemical and the solvent syntheses has also been carried out to determine the effects of various factors influencing the reactions. This is the first report on the mechanochemical synthesis of poly-NHC metal complexes as well as NHC-Rh complexes in ball mill.

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1. Introduction

N-heterocyclic carbenes or NHCs have proven themselves as most powerful tools in the domain of modern chemistry because of their outstanding potential and wide application in the field of organometallic/coordination chemistry, catalysis, photophysics, medicine and material science [1–5]. Hydroformylation and carbonylation were among the first processes realized with rhodium-NHC complexes as the catalysts [6–9]. Poly-NHCs, of which di-NHCs are the most common and abundant, have attained significant attractions in the last two decades due to their allowance to form various organometallic compounds with diversity in

geometries. They are relatively easy to synthesize and their properties can be modified simply by swapping the linker or changing the length of the linker, or placing various substituents onto the linker [2,10–13]. Transition metal complexes bearing NHCs as ligands have obtained widespread application in several fields of chemistry. Rh-NHC complexes deserve special mention due to their extensive usage in different domains of catalysis chemistry such as hydrogenation, dehydrogenation, hydroamination, hydration, C–C cross-coupling etc. [1–5,10,14–17]. Moreover, a recent study tells about the potential of Rh-NHC complexes as anticancer drugs [18].

A number of excellent articles on the synthesis of NHC-metal complexes are already available [3,14–17,19–26]. Still, the development of safer, more efficient and cleaner synthetic methodology is on high demand. From the viewpoint of green chemistry, synthetic methods under solvent-free or solvent-less conditions are of high desire as the energy-cost as well as the waste-production are

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reduced. The traditional solvent synthesis has a number of disadvantages such as long reaction time, high energy costs, furthermore it most often has a negative impact on the environment due to the prevalent usage of volatile organic solvents.

Mechanochemistry has a long history in the everyday life and in laboratory-scale chemical syntheses [27]. In the laboratory, mechanochemically assisted reactions are usually carried out either in planetary or in vibrating ball mills, where the reagents are loaded in a milling jar and movement of balls generates the mechanical force to the reagents [28,29]. The possibility to adjust several instrumental parameters makes the processes highly efficient and reproducible [30–32]. Nevertheless, in some cases simple grinding together of the solid reactants in a mortar with a pestle may also bring excellent results. Typically, such procedures require solvents only for the workup and purification of the products. In the last two decades a huge increase in the applications of such methods in chemical research could be seen, and the developments have been discussed in several recent reviews [28,33–37]. Today, mechanochemistry ranks amongst the top ten world changing technologies according to IUPAC [38]. In addition to introduction of grinding and milling into classical organic synthesis to allow the design of solvent-less procedures [39], mechanochemical syntheses have been more and more applied also in organometallic chemistry [34]. Procedures in controlled atmospheres (H_2 , CO, etc.) have been developed [40] and various techniques have been introduced to follow the reactions in situ for kinetic analysis of the syntheses [41]. With regard to the subject of our present study, the mechanochemical synthesis of Pd(II)- and Pt(II)-N-heterocyclic carbene complexes (with mortar and pestle, [42]) and the synthesis of Ag(I)-, Au(I)-, Cu(II)- and Pd(II)-NHC complexes (in ball mills, [43]) deserve special mention. In general, however, applications of mechanochemical methods for synthesis of important organometallic catalysts are still rare.

In the present work, azolium salts serving as precursors to several new $(-CH_2-)_n$ bridged ($n = 1$ or 4) diimidazole-2-ylidene ligands and their bridging dinuclear Rh(I)-complexes have been synthesized both via the classical solution synthesis and by solvent-free one-pot mechanochemical method and the results are compared. To the best of our knowledge, this is the first article to report the mechanochemical synthesis of di-NHC metal complexes as well as the first Rh–NHC complexes synthesized in ball-mill.

2. Results and discussion

2.1. General synthetic methods

To prepare the $(-CH_2-)_n$ bridged ($n = 1, 4$) substituted diimidazolium salts **2a,b** and **3a,b**, the corresponding unsubstituted diimidazoles **1a,b** were first synthesized following the literature [44,45]. Next, **1a,b** were reacted with the corresponding benzylic chlorides in 1:2 ratio as depicted in Scheme 1. All the bridging dinuclear rhodium(I) complexes **4a,b** and **5a,b** were prepared by reacting the diimidazolium chloride salts with $[RhCl(cod)]_2$ and K_2CO_3 in 1:1:10 ratio (Scheme 2).

Some of the diimidazolium salts (with various halide counterions) have been already applied for the preparation of gold (**2a**: [4]); palladium (**2a**: [46–48], **2b**: [46]); ruthenium (**2a**: [49,50], **2b**: [49]); and iridium (**2a**: [51]) NHC-ligated complexes. **3b** is also known from the literature, however, it was synthesized only as part of a rotaxane and with iodide as the counter ion [52]. All these previous syntheses were carried out in solution.

In our case, the classical solution synthesis of **2a,b** and **3a,b** as well as that of **4a,b** and **5a,b** involved heating of solutions of the reaction partners (Schemes 1 and 2) in the appropriate solvent for a period of time during which the reactions completed. Conversely,

the mechanochemical synthesis of the same compounds consisted of milling together the reaction partners in a planetary ball mill for the time sufficient to achieve high conversions; these reactions were carried out in air. The successful formation of Rh–NHC complexes was validated by the appearance of the characteristic Rh–C_{carbene} doublet signal(s) at δ 180–185 ppm with $J \approx 50$ Hz in the ^{13}C NMR spectra of the compounds. **4a,b** and **5a,b** are dinuclear Rh(I) complexes in which two $RhCl(cod)$ units are bridged by the appropriate carbene ligand derived from **2a,b** or **3a,b**. The presence of two rhodium centers was confirmed by the two doublet signals each in the region of δ 98–101 ppm and δ 68–71 ppm which are assigned to Rh–C_{vinyl} carbons of coordinated cod. Interestingly, in the mechanochemical syntheses described here, the dinuclear complexes **4a,b** and **5a,b** were exclusively obtained with no sign of chelate $[RhL]$ or macrocyclic $[Rh_2L_2]$ species which are known from solution syntheses [53,54]. HR ESI-MS measurements also confirmed the composition of the complexes. It should be added here, that none of the above ligands and complexes was obtained previously by mechanochemical synthesis.

2.2. Structural characterization by single crystal X-ray diffraction

The solid state structures of the carbene ligand precursors **3a**, and **3b**, and metal complexes **4a**, **4b** and **5b** have been determined by single crystal X-ray diffraction studies.

3a was dissolved in methanol in a small tube and saturated with KPF_6 . Then, in a closed container, the tube was half immersed into diethyl ether and stored at $-18^\circ C$. In four weeks, colourless crystals, suitable for XRD measurements, appeared on the wall of the tube. Crystals of **3b** were obtained from a methanolic solution layered with diethyl ether.

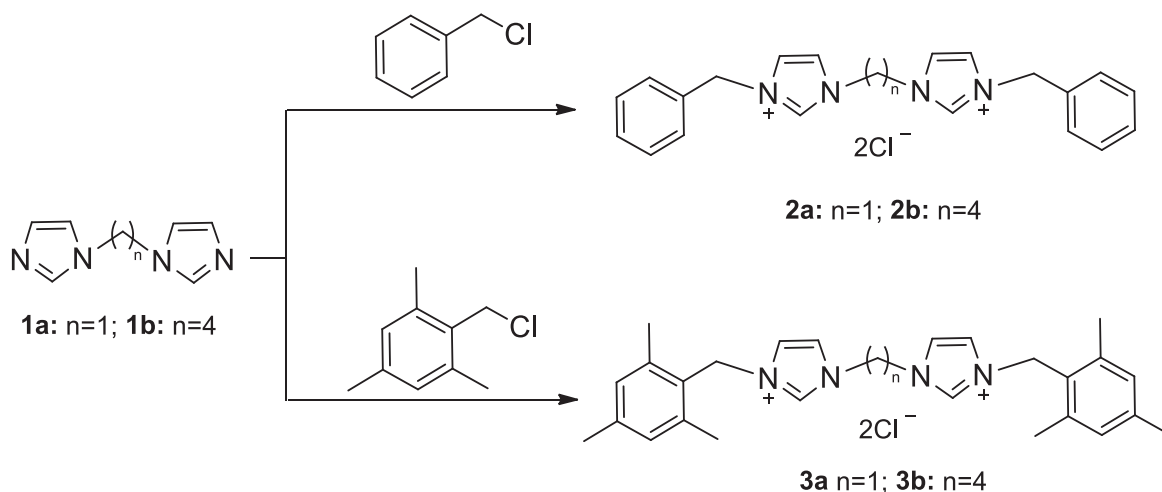
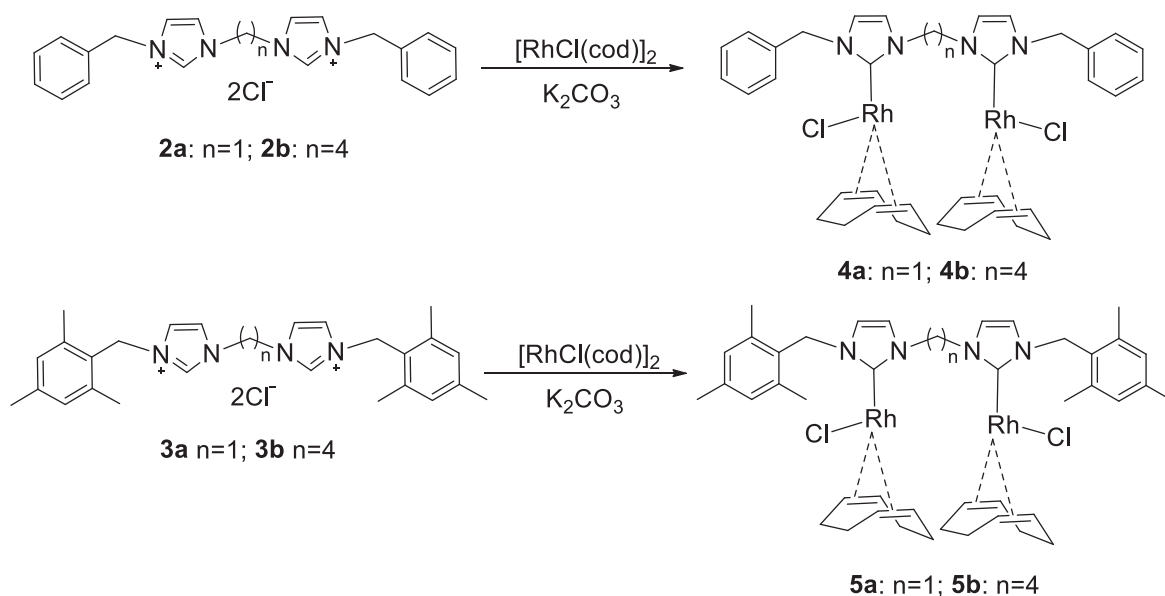
Both **3a** and **3b** crystallized as triclinic ($P\bar{1}$ space group). The asymmetric unit of **3a** contains a cationic NHC-precursor and two disordered PF_6^- ions and a methanol (Fig. 1) while that of **3b** contains half of the molecule and a chloride.

In the molecule of **3b**, the imidazole centroids are long apart (7.070 Å, Fig. S1); capped sticks representation is shown on Fig. 2. In the crystal, the molecules are packed in a stair-like arrangement (Fig. S2), in which the parallel imidazole ring planes are in a distance of 3.877 Å while the distance of the arene planes is 3.649 Å. All of the bond lengths and bond angles in the imidazole rings are as expected [55]. The supramolecular architecture is further stabilized by π - π stacking interactions between the five- and six-membered rings.

Selected bond lengths and angles: N1–C1:1.328(3) Å; N2–C1:1.378(3) Å; N3–C15:1.328(3) Å; N4–C15:1.326(3) Å; C2–C3:1.336(3) Å; C16 = C17:1.341(4) Å; N1–C14:1.355(3) Å; N3–C14:1.356(3) Å; N1–C1–N2:108.6(2)°; N1–C1–N2:108.1(2)°; N1–C14–N3:109.85(19)°; N2–C4–C5:113.6(2)°; N4–C18–C19:111.2(2)°.

Compound **2b** (as a dinitrate salt) in its co-crystal with $[Cu(NO_3)_2(H_2O)_2]$ has been previously studied by X-ray diffraction by Doimeadios [56]. Although the solid state structures of **3a**, and **3b**, discussed above, are very similar to that of **2b** published in Ref. [56], however, the bond lengths and angles cannot be quantitatively compared due to the large error of the structure of **2b** ($R_1 = 12.89\%$).

Crystallization of **5b** was attempted by several methods, unfortunately the best crystals (obtained by slow evaporation of its solution in CH_2Cl_2) were still of rather bad quality. **5b** crystallized in monoclinic $P2_1/n$ space group, the unit cell contains half of the molecule. After refinement of the best dataset, the error still remained large ($R_1 = 17.51\%$, $wR_2 = 41.25\%$) so while the molecular model (Fig. 3) proved to be suitable, the bond distances and bond angles cannot be evaluated.

Scheme 1. Synthesis of the carbene ligand precursors **2a,b** and **3a,b**.Scheme 2. Synthesis of the metal complexes **4a,b**, and **5a,b**.

The Rh(I)-complexes **4a** and **4b** were crystallized from benzene solutions layered with diethyl ether and were isolated as yellow crystals not sensitive to air and moisture. Both complexes crystallize in the monoclinic crystal system, however the space groups are different ($C2/c$ for **4a**, and $P2_1/c$ for **4b**). Capped sticks representations of the molecular structures are shown on Fig. 4, while the selected bond distances and angles can be found in Table 1.

There are only a few publications in the literature on the molecular structures of $[\{\text{RhCl}(\text{cod})\}_2(\mu\text{-di-NHC})]$ dinuclear Rh(I)-complexes [57–60]. Similar to the published structures, both **4a** and **4b** consist of two $\text{RhCl}(\text{cod})$ fragments connected by the methylene-, or butylene-bridged di-NHC ligands (Fig. 4). In **4a**, the $\text{Rh}-\text{C}_{\text{carbene}}$ bond distances are 2.0125(18) Å and 2.0261(16) Å, while in **4b** the same bonds are 2.030(3) Å and 2.025(3) Å long. These bond lengths are consistent with the typical $\text{Rh}-\text{C}_{\text{carbene}}$ distances in Rh(I)-NHC complexes, and refer to σ bonds with very little back-donation [55]. In **4a**, the two imidazole rings are at a dihedral angle of 87.47°, in contrast, in **4b**, these planes are almost

parallel with a dihedral angle of 7.84°.

In the crystal of **4a**, there are no interactions between the phenyl groups of the neighboring molecules, and the centroids of the imidazole rings are 3.719 Å and 5.021 Å apart (Fig. S3). In the case of **4b**, the flexibility of the butylene bridge allows π - π stacking interactions between the imidazole rings (their distance is 3.654 Å) and also between the phenyl rings with a distance of 4.534 Å (Figs. S4 and S5).

On the basis of the Rh1–Rh2 distances (6.938 Å in **4a** and 8.277 Å in **4b**) no Rh–Rh bonding interactions can be assumed in these complexes.

It has previously been observed, that the Rh(I)-complexes of di-NHC ligands with a methylene bridge and aliphatic N-substituents preferred chelate coordination [53,54]. In contrast, **4a** contains the N-benzyl-substituted di-NHC ligand (**2a**) in bridging position between the two $\text{RhCl}(\text{cod})$ moieties. Only two examples of similar structure have been determined so far [57,58].



Fig. 1. Capped sticks representation of the molecular structure of **3a** in the solid state (disordered PF_6^- counter ions and a methanol molecule are omitted for clarity).

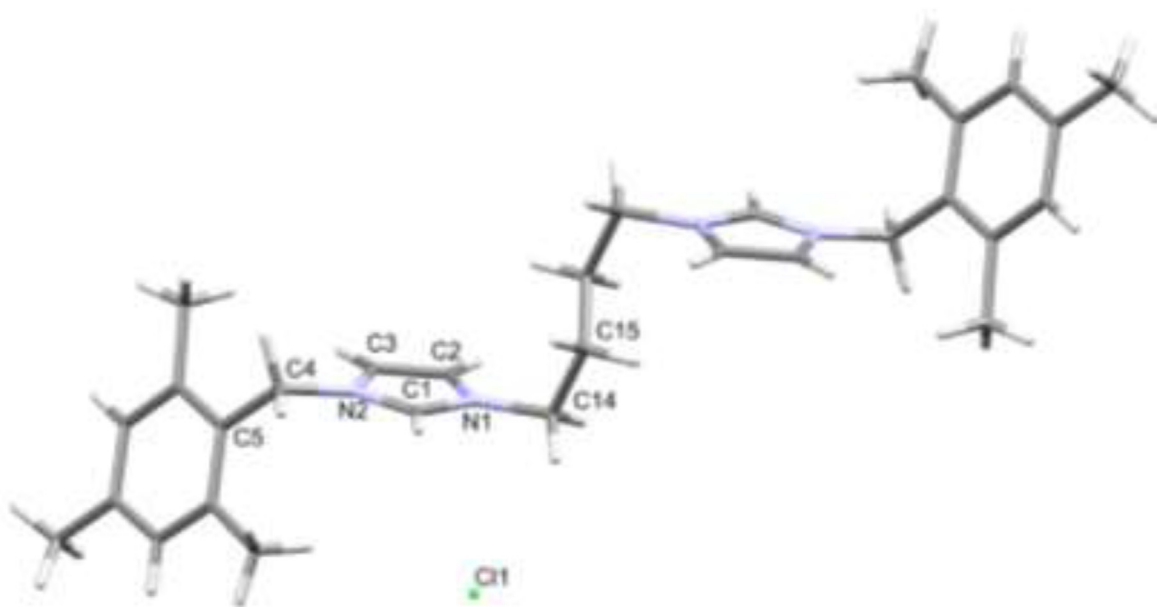


Fig. 2. Capped sticks representation of the molecular structure of **3b** in the solid state (counter ions are omitted for clarity). Selected bond lengths and angles: N1–C1:1.333(2) Å; N2–C1:1.327(2) Å; C2–C3:1.341(3) Å; N1–C1–N2:108.38(15)°; N2–C4–C5:112.10(14)°; N1–C14–C15:111.94(15)°.

2.3. Mechanochemical synthesis of diimidazolium salts **2a,b** and **3a,b** and the respective $[\{\text{RhCl}(\text{cod})\}_2(\mu\text{-di-NHC})]$ complexes **4a,b** and **5a,b**. Comparison to solution synthesis

The main aim of the present work was the exploration of the usefulness of mechanochemical synthesis in the field of Rh(I)–NHC complexes and its comparison to the solution methods of synthesis.

For this purpose, the syntheses were also carried out by using a planetary ball mill. Initially, the influence of ball milling conditions like milling time, frequency of milling and size of bearing balls were investigated (Tables 2 and 3). To do so, a milling cycle of 4 min (2 min milling, followed by another 2 min pause) to avoid the overheating, was used. Ligand **2b** (Table 2) was taken as reference, and 10 pieces of bearing balls with 5 mm diameter (in the

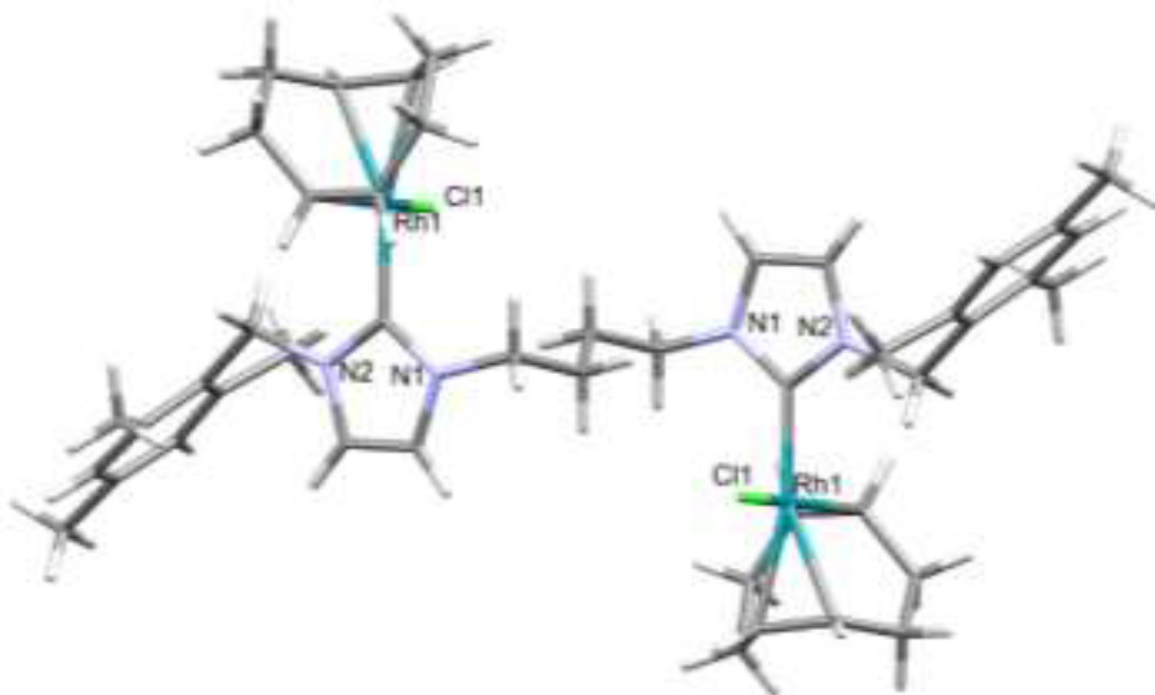


Fig. 3. Capped sticks representation of the molecular structure of **5b** in the solid state.

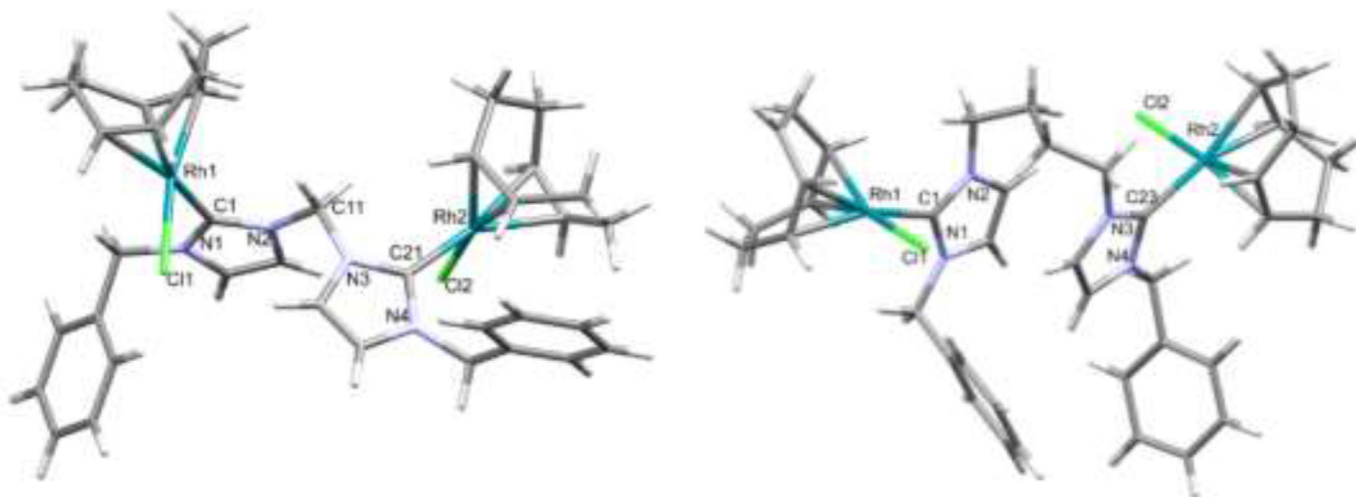


Fig. 4. Capped sticks representation of the molecular structure of the Rh(I)-complexes **4a** (left) and **4b** (right) in the solid state.

following: 10 Ø 5 mm) were employed to check the effects of frequency and milling time. The yield was found to be increased with the rise of frequency (Table 2, entries 2, 5) and after an initial increase, it levelled off with longer milling time (Table 2, entries 1–3). In contrast, the amount and the size of balls influenced significantly the yield (Table 2, entries 4–8). It was finally found that a mixture of 10 Ø 5 mm and 10 Ø 8 mm balls yielded the best result (71% isolated yield) after 90 cycles at 550 rpm frequency (Table 2, entry 8).

In the case of the metal complexes, **4b** was taken as a reference (Table 3) with 10 Ø 5 mm and 10 Ø 8 mm balls and the best yield (74%) was observed after 45 cycles at 550 rpm frequency (Table 3, entry 4). Under these optimized conditions, during the synthesis of **4b**, the outside surface temperature of the milling jar was regularly

checked with the use of a remote infrared thermometer. It was found that by the end of the 45th cycle (i.e. in 3 h reaction time), the surface temperature of the jar increased to 34.1 °C from 23.6 °C measured at the start of milling.

As the volume of the milling jar was fixed (12.5 mL), the influence of the amount of starting material for the preparation of diimidazolium salt **2b** from **1b**, and metal complex **4b** from **2b** was examined (Tables 4 and 5). It was observed that 100 mg of **1b** (Table 4, entry 2) and 150 mg of ligand precursor **2b** (Table 5, entry 3) as reactants resulted in the highest yields.

In addition, the influence of inert milling aids like quartz, silica, alumina and Celite Hyflo Supercel were also investigated. However, no positive influence was observed.

In the case of solution syntheses, the impact of reaction time and

Table 1

Selected bond lengths and bond angles for the solid state structures of the Rh(I)-complexes **4a** and **4b**.

	4a	4b
Rh1–C1	2.0125(18)	2.025(3)
Rh2–C21	2.0261(16)	2.030(3)
Rh1–Cl1	2.3775(4)	2.3808(8)
Rh2–Cl21	2.3828(15)	2.3669(18)
Rh1–Rh2	6.938	8.277
C2–C3	1.336(2)	1.336(4)
C22–C23	1.339(3)	1.332(4)
N2–C11–N3	110.60(3)	—
N1–C1–N2	103.91(13)	104.4(2)
N3–C21–N4	103.53(14)	104.1(2)
N1–C4–C5	112.08(14)	112.2(2)
N4–C24–C25	114.18(15)	113.2(2)
C1–Rh1–Cl1	88.79(4)	91.28(8)
C21–Rh2–Cl21	89.76(5)	89.36(8)

temperature were initially checked for the preparation of carbene ligand precursor **2b** and metal complex **4b** taken as references (Tables 6 and 7). According to the results, overnight reactions at high temperature (80 °C to reflux temperature; Table 6, entry 4; Table 7, entry 4) provided the best yields.

To compare the mechanochemical method with the classical solvent approach, the synthesis of **2b** and **4b** were carried out maintaining the same reaction time, i.e. 6 h for the preparation of diimidazolium salt **2b** (Table 2, entry 8 vs Table 6, entry 3) and 3 h for the synthesis of the Rh(I)-complex (Table 2, entry 4 vs Table 6, entry 3). The comparison clearly shows that the ball mill synthesis results in higher yields than the solution method (71% vs 49% for the carbene precursor **2b**; and 74% vs 18% for complex **4b**). In addition, since the mechanochemical synthesis requires solvents only for extraction and purification, the overall solvent need is significantly reduced – up to 50% in the small scale syntheses of ligands and complexes described in this study (see Experimental part).

Table 2

Optimization of milling conditions for the synthesis of **2b**^a from **1b** and benzyl chloride.

Entry	Diameter of balls (Ø mm)	Number of balls	Frequency (rpm)	Cycles ^b	Yield (%) ^c
1	5	10	350	45	42
2	5	10	350	90	58
3	5	10	350	135	59
4	5	10	550	90	65
5	5	20	550	90	68
6	8	10	550	90	67
7	8	20	550	90	70
8	5 + 8	10 + 10	550	90	71

^a Synthesis was performed with 0.526 mmol of **1b** and 1.05 mmol of benzyl chloride in air.

^b 1 cycle = 2 min milling + 2 min pause.

^c Isolated yield.

Table 3

Optimization of milling conditions for the synthesis of metal complex **4b**^a.

Entry	Diameter of balls (Ø mm)	Number of balls	Frequency (rpm)	Cycles ^b	Yield (%) ^c
1	5 + 8	10 + 10	350	45	69
2	5 + 8	10 + 10	350	90	71
3	5 + 8	10 + 10	350	135	72
4	5 + 8	10 + 10	550	45	74

^a Synthesis was performed with 0.338 mmol of **2b**, 0.338 mmol of [RhCl(cod)]₂ and 3.38 mmol of K₂CO₃ in air.

^b 1 cycle = 2 min milling + 2 min pause.

^c Isolated yield.

Table 4

Effect of the reactant amount for the formation of ligand **2b**^a in its mechanochemical synthesis from **1b** and benzyl chloride.

Entry	Amount of 1b (mg)	Yield (%) ^b
1	50	58
2	100	71
3	150	68
4	200	62

^a Reactions were performed with **1b** and benzyl chloride (2 mol equivalent), ball mill, mixed Ø 5 and Ø 8 mm balls, 550 rpm, 90 cycles.

^b Isolated yield.

3. Conclusion

Convenient and efficient novel mechanochemical methods of synthesis for two (–CH₂–)_n-bridged diimidazolium salts (precursors to di-NHC ligands) and four bridging dinuclear rhodium(I)–N-heterocyclic carbene complexes of the type [{RhCl(cod)}₂(μ-di-NHC)] were developed which are characterized with shorter reaction times and substantially reduced need of organic solvents compared to the classical solution syntheses of the same compounds. Together with the simplicity of the procedure, zero-solvent condition, and possible multipurpose applications, directed us to the conclusion that the mechanochemical (ball mill) synthesis of metal complexes in several cases may prove superior in comparison to the classical solution synthesis approach. In addition, the solid state structures of two new diimidazolium salts (**3a** and **3b**) and three of the new [{RhCl(cod)}₂(μ-di-NHC)] complexes, **4a**, **4b**, **5b** were determined by single crystal X-ray diffraction.

4. Experimental

4.1. General information

The Rh-metal precursor [RhCl(cod)]₂ was prepared as described in Ref. [61]. Synthesis of 1,1'-di(imidazole-1-yl)methane, **1a** and 1,4-di(imidazole-1-yl)butane, **1b** were done according to the literature

Table 5

Effect of the reactant amount for the formation of metal complex **4b**^a in its mechanochemical synthesis from **2b** and [RhCl(cod)]₂.

Entry	Amount of 2b (mg)	Yield (%) ^b
1	50	61
2	100	67
3	150	74
4	200	70

^a Reactions were performed with **2b**, [RhCl(cod)]₂ (1 mol equivalent) and K₂CO₃ (10 mol equivalent), ball mill, mixed Ø 5 and Ø 8 mm balls, 550 rpm 90 cycles.

^b Isolated yield.

Table 6

Effect of the reaction temperature and time for the formation of **2b** in its solution synthesis from **1b** and benzyl chloride.^a

Entry	Temperature (°C)	Time (h)	Yield (%) ^b
1	room temperature	6	0
2	50	6	6
3	reflux temperature	6	49
4	reflux temperature	overnight	76

^a Reaction was performed in acetonitrile (5 mL) with 0.526 mmol of **1b** and 1.05 mmol of benzyl chloride.

^b Isolated yield.

[44,45]. 1,1'-methylene-bis(3-benzyl-imidazolium)dichloride, **2a** [62] and 1,1'-(butane-1,4-diyl)bis(3-benzyl-imidazolium)dichloride, **2b** [46] are known compounds, however, in addition to the traditional solvent synthesis, we obtained them also in reactions in a ball mill. The identity and purity of these four compounds were checked by correlating their respective ¹H, ¹³C and ESI-MS spectra to those available in the literature.

All other chemicals and solvents were purchased from Sigma-Aldrich, Alpha Aesar, Merck, Molar Chemicals Kft. and VWR International and employed as received without further purification. Analytical thin-layer chromatography (TLC) was carried out on Kieselgel 60 F254 plates from Merck and the plates were visualised under UV fluorescence light at 254 nm. The column chromatography was executed on silica gel from Sigma-Aldrich (70–230 mesh, 63–200 µm).

Reactions in ball mill were carried out with the use of a planetary milling instrument model 'RETSCH PM 100' with a stainless steel jar (12.5 mL) and G100 ball bearings (Ø 5 mm and Ø 8 mm) operated at room temperature. In the generally used protocol, 1 cycle consisted of 2 min milling followed by 2 min cooling at ambient temperature; after an initial warming period the stabilized temperature of the milling jar in a 45 cycles procedure was around 34 °C, estimated by the use of a remote infrared thermometer.

¹H and ¹³C{¹H} NMR spectra were recorded at room temperature on a Bruker DRX 360 instrument. MeOD (δ = 49.15 ppm) and CD₂Cl₂ (δ = 54.00 ppm) were used as ¹³C NMR internal standards for the ligands and for the metal complexes, respectively, while the ¹H NMR spectra were referenced to TMS and residual non-

Table 7

Effect of the reaction temperature and time for the formation of metal complex **4b** in its solution synthesis from **2b** and [RhCl(cod)]₂.^a

Entry	Temperature (°C)	Time (h)	Yield (%) ^b
1	room temperature	3	0
2	50	3	0
3	80	3	18
4	80	overnight	77

^a Reaction was performed in toluene (10 mL) with 0.338 mmol of **2b**, 0.338 mmol of [RhCl(cod)]₂ and 3.38 mmol of K₂CO₃.

^b Isolated yield.

deuterated solvent peaks. High-resolution electrospray ionization mass spectra (HR ESI-MS) were recorded on a Bruker maXis II MicroTOF-Q type Qq-TOF-MS instrument and controlled by Compass Data Analysis 4.4 software from Bruker. CHN elemental analysis was done using an Elementar Vario Micro microanalyzer.

Single crystals were examined on a Bruker D8 Venture diffractometer (SC-XRD) and data processing was managed by Olex² software [63] including SHELX programs [64]. The molecular images were prepared by the Mercury CSD-4.3.0 software [65]. The crystallographic data (excluding the structure factors) for **3a**, **3b**, **4a**, **4b**, **5b** were deposited at Cambridge Crystallographic Data Centre, as CCDC-1990551 and 1981017–1981020.

4.2. Synthesis of 1,1'-methylene-bis(3-benzyl-imidazolium)dichloride (**2a**) and 1,1'-(butane-1,4-diyl)bis(3-benzyl-imidazolium)dichloride (**2b**)

2a and **2b** were synthesized in a slightly modified, more convenient way than described earlier [46,62]. (For characterization see Supplementary Material).

4.2.1. Solution synthesis

A mixture of **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and benzyl chloride (for **1a**: 155 µL, 1.35 mmol; for **1b**: 121 µL, 1.052 mmol) was dissolved in CH₃CN (5 mL) in a Schlenk tube and stirred overnight under reflux temperature until the appearance of a white precipitate. The resulting hot solution was filtered and the precipitate was washed with 2 × 5 mL cold CH₃CN, and once with 5 mL acetone, respectively, and then dried under vacuum. White powder. Yield: 78% for **2a** (211 mg); 76% for **2b** (177 mg).

4.2.2. Mechanochemical synthesis

A 12.5 mL ball milling jar was charged with 10 Ø 5 mm and 10 Ø 8 mm stainless steel balls, **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and benzyl chloride (for **1a**: 155 µL, 1.35 mmol; for **1b**: 121 µL, 1.052 mmol). The mixtures were milled over a period of 90 cycles (1 cycle = 2 min milling + 2 min pause) at 550 rpm. Afterwards, the jar and the bearing balls were washed twice with 5 mL methanol and the resulting solution was filtered through Celite Hyflo Supercel. Evaporation of methanol yielded **2a** (74%, 199 mg) or **2b** (71%, 165 mg) as a white powder.

4.3. Synthesis of 1,1'-methylene-bis(3-(2,4,6-trimethylbenzyl)imidazolium)dichloride (**3a**) and 1,1'-(butane-1,4-diyl)bis(3-(2,4,6-trimethylbenzyl)imidazolium)dichloride (**3b**)

4.3.1. Solution synthesis

A mixture of **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and 2-(chloromethyl)-1,3,5-trimethylbenzene (for **1a**: 228 mg, 1.35 mmol; for **1b**: 177 mg, 1.052 mmol) was dissolved in CH₃CN (5 mL) in a Schlenk tube and stirred overnight under reflux temperature until the appearance of a white precipitate. The resulting hot solution was filtered and the precipitate was washed with 2 × 5 mL cold CH₃CN, and once with 5 mL acetone, respectively, and dried under vacuum. White powder. Yield: 70% for **3a** (228 mg) and 86% for **3b** (238 mg).

4.3.2. Mechanochemical synthesis

A 12.5 mL ball milling jar was charged with 10 Ø 5 mm and 10 Ø 8 mm stainless steel balls, **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and 2-(chloromethyl)-1,3,5-trimethylbenzene (for **1a**: 228 mg, 1.35 mmol; for **1b**: 177 mg, 1.052 mmol). The mixtures were milled over a period of 90 cycles (1 cycle = 2 min milling + 2 min pause) at 550 rpm. Afterwards, the jar and the

bearing balls were washed with 2×5 mL methanol and the resulting solution was filtered through Celite Hyflo Supercel. Evaporation of methanol yielded **3a** (68%, 222 mg) or **3b** (78%, 216 mg) as a white powder.

4.3.2.1. 3a. ^1H NMR (360 MHz, MeOD), δ/ppm : 9.45 (s, 2H, NCHN), 8.21 (s, 2H, CH_{imid}), 7.79 (s, 2H, CH_{imid}), 7.23 (s, 4H, CH_{Ar}), 6.89 (s, 2H, NCH₂N), 5.74 (s, 4H, ArCH₂N), 2.53 (18H, CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, MeOD), δ/ppm : 140.17 (NCN_{imid}), 138.52 (C_{Ar}), 129.76 (CH_{Ar}), 125.46 (C_{Ar}), 123.32 (CH_{imid}), 122.58 (CH_{imid}), 58.88 (NCH₂N), 48.18 (ArCH₂N), 19.97 (CH₃), 18.56 (CH₃);

Elemental analysis: Calc. for: $\text{C}_{27}\text{H}_{34}\text{N}_4\text{Cl}_2 \times 4.5\text{H}_2\text{O}$: C, 57.24; H, 7.65; N, 9.89. Found: C, 57.38; H, 6.89; N, 11.56;

HR ESI-MS: m/z for $[\text{M} - 2\text{Cl}, \text{H}]$: Calculated: 413.2700, Found: 413.2700.

4.3.2.2. 3b. ^1H NMR (360 MHz, MeOD), δ/ppm : 9.09 (s, 2H, NCHN), 7.91 (s, 2H, CH_{imid}), 7.63 (s, 2H, CH_{imid}), 7.21 (s, 4H, CH_{Ar}), 5.68 (s, 4H, ArCH₂N), 4.48 (s, 4H, N-CH₂-CH₂-CH₂-CH₂-N), 2.51 (18H, CH₃), 2.12 (s, 4H, N-CH₂-CH₂-CH₂-CH₂-N);

$^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, MeOD), δ/ppm : 139.88 (NCN_{imid}), 138.36 (C_{Ar}), 135.74 (C_{Ar}), 129.72 (CH_{Ar}), 126.07 (C_{Ar}), 122.82 (CH_{imid}), 122.33 (CH_{imid}), 48.93 (-CH₂-CH₂-CH₂-CH₂-), 47.63 (ArCH₂N), 26.82 (-CH₂-CH₂-CH₂-CH₂-), 20.02 (CH₃), 18.61 (CH₃);

Elemental analysis: Calc. for $\text{C}_{30}\text{H}_{40}\text{N}_4\text{Cl}_2 \times 4.5\text{H}_2\text{O}$: C, 59.20; H, 8.11; N, 9.21. Found: C, 59.27; H, 8.05; N, 9.41;

HR ESI-MS: m/z for $[\text{M} - \text{Cl}]$: Calculated: 491.2936, Found: 491.2935.

4.4. Synthesis of bridging di-nuclear Rh(I)-metal complexes **4a, 4b, 5a, 5b**

4.4.1. Solution synthesis

150 mg of **2a** (0.374 mmol) or **2b** (0.338 mmol) or **3a** (0.309 mmol) or **3b** (0.284 mmol) was dissolved in 10 mL of toluene in a Schlenk tube under inert atmosphere followed by the addition of $[\text{RhCl}(\text{cod})]_2$ (for **2a**: 184 mg, 0.374 mmol; for **2b**: 167 mg, 0.338 mmol; for **3a**: 152 mg, 0.309 mmol; for **3b**: 140 mg, 0.284 mmol) and K_2CO_3 (for **2a**: 517 mg, 3.74 mmol; for **2b**: 467 mg, 3.38 mmol; for **3a**: 427 mg, 3.09 mmol; for **3b**: 392 mg, 2.84 mmol) in one portion. The solutions were stirred overnight at 80 °C; the final conversion was checked with TLC. The resulting solutions were then filtered, the residues were washed with 2×5 mL toluene and the filtrates were collected. The combined filtrates were evaporated to dryness and the residues were purified using silica gel column chromatography with a CH_2Cl_2 and EtOAc mixture (1:1) as eluent and dried under vacuum. Yellow powders. Yield 80% for **4a** (245 mg), 77% for **4b** (224 mg), 51% for **5a** (143 mg) and 65% for **5b** (174 mg).

4.4.2. Mechanochemical synthesis

A 12.5 mL ball milling jar was charged with 10 \emptyset 5 mm and 10 \emptyset 8 mm stainless steel balls, 150 mg of **2a** (0.374 mmol) or **2b** (0.338 mmol) or **3a** (0.309 mmol) or **3b** (0.284 mmol), $[\text{RhCl}(\text{cod})]_2$ (for **2a**: 184 mg, 0.374 mmol; for **2b**: 167 mg, 0.338 mmol; for **3a**: 152 mg, 0.309 mmol; for **3b**: 140 mg, 0.284 mmol) and K_2CO_3 (for **2a**: 517 mg, 3.74 mmol; for **2b**: 467 mg, 3.38 mmol; for **3a**: 427 mg, 3.09 mmol; for **3b**: 392 mg, 2.84 mmol) and the mixtures were milled over a period of 45 cycles (1 cycle = 2 min milling + 2 min pause) at 550 rpm. Afterwards, the jar and the bearing balls were washed with 2×5 mL dichloromethane and the resulting solutions were filtered. The filtrates were evaporated to dryness, and the residues were purified using silica gel column chromatography with a CH_2Cl_2 and EtOAc mixture (1:1) as eluent and dried under vacuum. Yellow powders. Yield 71%, for **4a** (218 mg), 74% for **4b**

(215 mg), 58% for **5a** (162 mg) and 69% for **5b** (185 mg).

4.4.2.1. 4a. ^1H NMR (360 MHz, CD_2Cl_2), δ/ppm : 7.98 (s, 2H, CH_{imid}), 7.66 (s, 2H, CH_{imid}), 7.43 (s, 10H, CH_{Ar}), 6.75 (s, 2H, NCH₂N), 5.87 (s, 4H, ArCH₂N), 5.14–5.13 (m, 4H, cod-CH_{vinyl}), 3.50 (s, 2H, cod-CH_{vinyl}), 3.34 (s, 2H, cod-CH_{vinyl}), 2.67–1.82 (m, 16H, cod-CH_{allyl});

$^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm : 184.23 (d, $^1J_{\text{Rh}-\text{C}} = 51.9$ Hz, NCN_{imid}), 136.39 (C_{Ar}), 128.79 (CH_{Ar}), 128.03 (CH_{Ar}), 122.05 (CH_{imid}), 121.50 (CH_{imid}), 99.84 (d, $J = 5.9$ Hz, cod-CH_{vinyl}), 99.20 (d, $J = 6.6$ Hz, cod-CH_{vinyl}), 69.73 (d, $^1J_{\text{Rh}-\text{C}} = 13.8$ Hz, cod-CH_{vinyl}), 68.64 (d, $^1J_{\text{Rh}-\text{C}} = 13.8$ Hz, cod-CH_{vinyl}), 63.31 (NCH₂N), 54.58 (ArCH₂N), 33.62 (cod-CH_{allyl}), 32.17 (cod-CH_{allyl}), 29.20 (cod-CH_{allyl}), 28.40 (cod-CH_{allyl});

Elemental analysis. Calc. for $\text{C}_{37}\text{H}_{44}\text{N}_4\text{Cl}_2\text{Rh}_2$: C, 54.10; H, 5.40; N, 6.82. Found: C, 54.22; H, 5.55; N, 6.76;

HR ESI-MS: m/z for $[\text{M} - \text{Cl}]$: Calculated: 785.1359, Found: 785.1357.

4.4.2.2. 4b. ^1H NMR (360 MHz, CD_2Cl_2), δ/ppm : 7.45–7.33 (m, 4H, CH_{imid} + 10H, CH_{Ar}), 7.13 (d, $^1J_{\text{H}-\text{H}} = 1.80$ Hz, 1H, N-CH₂-CH₂-CH₂-CH₂-N), 7.04 (d, $^1J_{\text{H}-\text{H}} = 1.80$ Hz, 1H, N-CH₂-CH₂-CH₂-CH₂-N), 6.77 (d, $^1J_{\text{H}-\text{H}} = 1.80$ Hz, 1H, N-CH₂-CH₂-CH₂-CH₂-N), 6.54 (d, $^1J_{\text{H}-\text{H}} = 1.80$ Hz, 1H, N-CH₂-CH₂-CH₂-CH₂-N), 5.99 (d, $^1J_{\text{H}-\text{H}} = 14.76$ Hz, 2H, ArCH₂N), 5.69–5.57 (m, 2H, ArCH₂N), 4.98–4.88 (m, 4H, cod-CH_{vinyl}), 4.86–4.82 (m, 2H, cod-CH_{vinyl}), 4.45–4.32 (s, 2H, cod-CH_{vinyl}), 2.54–2.35 (m, 8H, cod-CH_{allyl}), 2.23 (s, 4H, N-CH₂-CH₂-CH₂-CH₂-N), 2.01–1.94 (m, 8H, cod-CH_{allyl});

$^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm : 182.67 (d, $^1J_{\text{Rh}-\text{C}} = 51.2$ Hz, NCN_{imid}), 182.21 (d, $^1J_{\text{Rh}-\text{C}} = 50.6$ Hz, NCN_{imid}), 136.91 (C_{Ar}), 136.89 (C_{Ar}), 128.71 (CH_{Ar}), 128.68 (CH_{Ar}), 128.36 (CH_{Ar}), 128.22 (CH_{Ar}), 127.95 (CH_{Ar}), 121.30 (CH_{imid}), 121.28 (CH_{imid}), 120.45 (CH_{imid}), 120.35 (CH_{imid}), 98.21 (d, $^1J_{\text{Rh}-\text{C}} = 6.61$, cod-CH_{vinyl}), 98.18 (d, $^1J_{\text{Rh}-\text{C}} = 6.61$, cod-CH_{vinyl}), 98.04–97.88 (m, cod-CH_{vinyl}), 68.64 (d, $^1J_{\text{Rh}-\text{C}} = 13.77$, cod-CH_{vinyl}), 68.60 (d, $^1J_{\text{Rh}-\text{C}} = 13.78$, cod-CH_{vinyl}), 67.96 (d, $^1J_{\text{Rh}-\text{C}} = 13.79$, cod-CH_{vinyl}), 67.92 (d, $^1J_{\text{Rh}-\text{C}} = 13.79$ Hz, cod-CH_{vinyl}), 54.55 (ArCH₂N), 54.48 (ArCH₂N), 50.34 (-CH₂-CH₂-CH₂-CH₂-), 50.25 (-CH₂-CH₂-CH₂-CH₂-), 32.95–32.86 (m, cod-CH_{allyl}), 29.03 (-CH₂-CH₂-CH₂-CH₂-), 28.95 (cod-CH_{allyl}), 28.68 (cod-CH_{allyl}), 27.95 (cod-CH_{allyl}), 27.52 (cod-CH_{allyl});

Elemental analysis. Calc. for $\text{C}_{40}\text{H}_{50}\text{N}_4\text{Cl}_2\text{Rh}_2 \times 0.5\text{H}_2\text{O}$: C, 55.06; H, 5.89; N, 6.42. Found: C, 52.26; H, 5.81; N, 6.30;

HR ESI-MS: m/z for $[\text{M} - \text{Cl}]$: Calculated: 827.1829, Found: 827.1828.

4.4.2.3. 5a. ^1H NMR (360 MHz, CD_2Cl_2), δ/ppm : 7.76 (d, $^1J_{\text{H}-\text{H}} = 1.80$ Hz, 2H, CH_{imid}), 7.52 (s, 2H, CH_{imid}), 6.93 (s, 4H, CH_{Ar}), 6.23 (d, $^1J_{\text{H}-\text{H}} = 2.05$ Hz, 2H, NCH₂N), 5.85 (d, $^1J_{\text{H}-\text{H}} = 14.08$ Hz, 2H, ArCH₂N), 5.46 (d, $^1J_{\text{H}-\text{H}} = 14.08$ Hz, 2H, ArCH₂N), 5.09–5.00 (m, 2H, cod-CH_{vinyl}), 4.98–4.96 (m, 2H, cod-CH_{vinyl}), 3.51–3.49 (m, 4H, cod-CH_{vinyl}), 2.59–2.36 (m, 6H, cod-CH_{allyl}), 2.29 (s, 6H, CH₃), 2.27 (s, 12H, CH₃), 2.16–1.96 (m, 10H, cod-CH_{allyl});

$^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm : 183.44 (d, $^1J_{\text{Rh}-\text{C}} = 50.55$ Hz, NCN_{imid}), 138.62 (C_{Ar}), 138.38 (C_{Ar}), 129.34 (CH_{Ar}), 127.98 (C_{Ar}), 120.58 (CH_{imid}), 120.16 (CH_{imid}), 99.52 (d, $^1J_{\text{Rh}-\text{C}} = 6.61$ Hz, cod-CH_{vinyl}), 99.02 (d, $^1J_{\text{Rh}-\text{C}} = 6.61$ Hz, cod-CH_{vinyl}), 69.7 (d, $^1J_{\text{Rh}-\text{C}} = 14.44$ Hz, cod-CH_{vinyl}), 67.82 (d, $^1J_{\text{Rh}-\text{C}} = 14.44$ Hz, cod-CH_{vinyl}), 63.92 (NCH₂N), 48.76 (ArCH₂N), 33.59 (cod-CH_{allyl}), 32.44 (cod-CH_{allyl}), 29.18 (cod-CH_{allyl}), 28.50 (cod-CH_{allyl}), 20.74 (CH₃), 19.81 (CH₃);

Elemental analysis. Calc. for $\text{C}_{43}\text{H}_{56}\text{N}_4\text{Cl}_2\text{Rh}_2 \times 4.5\text{H}_2\text{O}$: C, 52.34.03; H, 6.64; N, 5.68. Found: C, 52.10; H, 5.64; N, 5.74;

HR ESI-MS: m/z for $[\text{M} - \text{Cl}]$: Calculated: 869.2298, Found: 869.2303.

4.4.2.4. **5b**. ^1H NMR (360 MHz, MeOD), δ /ppm: 6.99–6.91 (m, 2H, $\text{CH}_{\text{imid}} + 4\text{H}$, CH_{Ar}), 6.27 (d, $^1J_{\text{H-H}} = 1.84$ Hz, 1H, CH_{imid}), 6.18 (s, $^1J_{\text{H-H}} = 1.84$ Hz, 1H, CH_{imid}), 5.90–5.83 (m, 2H, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 5.49–5.45 (m, 2H, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 4.99–4.97 (m, 4H, CH_{Ar}), 4.87–4.77 (m, 2H, $\text{cod-CH}_{\text{vinyl}}$), 4.42–4.32 (m, 2H, $\text{cod-CH}_{\text{vinyl}}$), 3.56–3.52 (m, 2H, $\text{cod-CH}_{\text{vinyl}}$), 3.42–3.37 (m, 2H, $\text{cod-CH}_{\text{vinyl}}$), 2.55–2.39 (m, 8H, $\text{cod-CH}_{\text{allyl}}$), 2.33–2.28 (m, 18H, CH_3), 2.19–1.99 (m, 4H, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 2.04–1.97 (m, 8H, $\text{cod-CH}_{\text{allyl}}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (90 MHz, CD_2Cl_2), δ /ppm: 181.86 (d, $^1J_{\text{Rh-C}} = 50.55$ Hz, NCN_{imid}), 181.63 (d, $^1J_{\text{Rh-C}} = 50.54$ Hz, NCN_{imid}), 138.46 (C_{Ar}), 129.22 (CH_{Ar}), 128.38 (C_{Ar}), 119.97 (CH_{imid}), 118.97 (CH_{imid}), 118.87 (CH_{imid}), 97.92 (d, $^1J_{\text{Rh-C}} = 6.57$, $\text{cod-CH}_{\text{vinyl}}$), 97.88–97.75 (m, $\text{cod-CH}_{\text{vinyl}}$), 67.87 (d, $^1J_{\text{Rh-C}} = 14.45$ Hz, $\text{cod-CH}_{\text{vinyl}}$), 67.84 (d, $^1J_{\text{Rh-C}} = 13.79$ Hz, $\text{cod-CH}_{\text{vinyl}}$), 67.81 (d, $^1J_{\text{Rh-C}} = 14.45$ Hz, $\text{cod-CH}_{\text{vinyl}}$), 50.56 ($-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 50.44 ($-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 48.71 (ArCH_2N), 48.67 (ArCH_2N), 33.27 ($\text{cod-CH}_{\text{allyl}}$), 33.21 ($\text{cod-CH}_{\text{allyl}}$), 29.19 ($\text{cod-CH}_{\text{allyl}}$), 29.07 ($\text{cod-CH}_{\text{allyl}}$), 28.63 ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$), 27.98 ($\text{cod-CH}_{\text{allyl}}$), 27.77 ($\text{cod-CH}_{\text{allyl}}$), 20.76 (CH_3), 19.76 (CH_3), 19.73 (CH_3);

Elemental analysis. Calc. for $\text{C}_{46}\text{H}_{62}\text{N}_4\text{Cl}_2\text{Rh}_2 \times 0.5\text{H}_2\text{O}$: C, 57.75; H, 6.64; N, 5.86. Found: C, 57.61; H, 6.54; N, 5.68;

HR ESI-MS: m/z for $[\text{M} - \text{Cl}]$: Calculated: 911.2768, Found: 911.2751.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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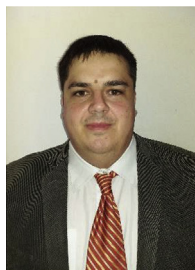
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